PACKAGING AND FOOD INTERACTIONS MODELING: VALIDATION FOR COMPLIANCE WITH SPECIFIC MIGRATION REGULATIONS

Iván D. López, Juan C. Estefan, Alejandro Betancur
ICIPC - Instituto de Capacitación e Investigación del Plástico y del Caucho, Medellín - Colombia

Abstract

A validation model for compliance with specific migration regulations based on the EU standard 10/2011 about plastic materials and articles intended to come into contact with food will be presented. This article describes the implementation of the numerical model used for the migration calculation, which is validated by comparing it to other models available in the state of art. A case study is presented to show the benefits of this model.

Introduction

Monomers, additives, oligomers and solvents migrate from polymeric packaging into food [1]. These migrants may affect taste and food safety.

Because of concerns about food safety, migration is highly regulated [2, 3, 4, 5]. The policy of these regulations is to use positive lists as constraints, which limit the use of potentially toxic substances and determine the limits of overall and specific migration, in order to ensure the safety of the consumer.

The most important migration regulations are EU 10/2011, of the European Union, and Title 21, of the United States FDA. These regulations are completely different. Title 21 assumes substances that are part of the package are indirect food additives. However, EU 10/2011 is based on a defined migration limit for substances into food; if the migration value is greater than the limit, the substance has the potential to affect the health of consumers.

The EU 10/2011 regulation is widely used in the industry and is the basis of other regulations, making this a very important topic to study.

The measurement of overall migration uses recognized and relatively easy-to-implement gravimetric methods [6, 7, 8, 9], while specific migration involves the development, implementation and validation of more sophisticated and sensitive analytical techniques such as high performance liquid chromatography (HPLC), gas chromatography (GC), UV-Visible spectroscopy and nuclear magnetic resonance (NMR) [10].

These techniques are very expensive, and in order to save time and money, mathematical methods become a good option [11, 12]. These models predict the migration of low molecular weight substances using the laws of mass diffusion under extreme conditions, ensuring that measurements of real migration do not exceed the theoretical calculations [13].

Currently, in Europe, theoretical calculations of migration are permitted as an alternative to conventional analysis methods. Directive 90/128/EEC (2001) in its sixth amendment endorses the use of "generally recognized diffusion models" as an alternative to conventional analysis [14].

The model introduced in this article, offers the following advantages in comparison with others found in the state of art [15] [16]:

- Uses convective boundary conditions to avoid underprediction of migration
- Helps to classify foods according to the families defined by EU regulation 10/2011
- Determines the time and temperature of the migration test following the guidelines of EU Regulation 10/2011, depending on the shelf life chosen
- Assigns food simulants according to EU Regulation 10/2011, depending on the food family chosen
- Estimates the fat reduction factor (FRF) automatically according to the relationship between Migrant – Simulant – Food Family
- Performs Migrant – Simulant analysis, evaluating in each case if the specific migration limit (SML) is exceeded
- Considers that the sum of specific migration in the problem cannot exceed the overall migration limit
- Considers the migration limit by group as defined in EU Regulation 10/2011

In order to consider in detail all the guidelines of the EU Regulation 10/2011, a database with all information concerning food families, migrants, simulants and basic polymers in packaging is used by the model. The addition of further material and migrants is allowed.

In this article, the numerical implementation of the model is detailed and is evaluated by comparing the results obtained with available models. Finally a case study is presented to show the benefits of our model.

Numerical Implementation

Given a structure of m layers as shown in Figure 1 and assuming a perfect contact between them, it is possible to discretize each k layer in n points as shown in Figure 2.

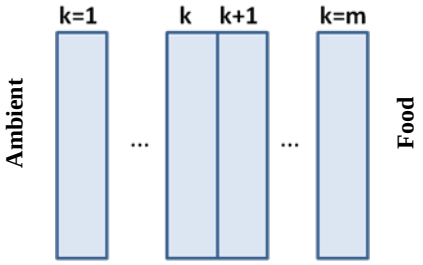

Figure 1 Multi layer structure scheme

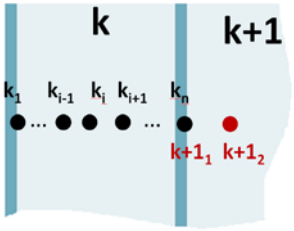

Figure 2 Each layer is discretized by finite differences

For internal nodes $(k_1 < k_i < k_n)$, the governing equation is given by Fick's second law:

$$\frac{\partial c_{k_i}}{\partial t} = D_k \frac{\partial^2 c_{k_i}}{\partial x^2} \tag{1}$$

Where c_{k_i} is the concentration of the migrant in layer k at the node i, D_k is the diffusivity of the migrant in the material of layer k and is defined by the Piringer equation [17]:

$$D_k = D_0 e^{\left(A_{p_k}{}' - \frac{\tau_k}{T} - 0.1351 M_w{}^{2/3} + 0.003 M_w - \frac{10454}{T}\right)} \tag{2}$$

This model considers migrant and polymer dependency. M_w is the molecular weight of the migrant, T is the storage temperature, and D_0, $A_{p_k}{}'$ and τ_k are parameters of the model and are polymer dependents.

By expressing the equation in a dimensionless way and solving by implicit finite differences,

$$c_{k_{i-1}}^{j+1}\left(-\frac{1}{\Delta x^2}\right) + c_{k_i}^{j+1}\left(\frac{\Pi_{1_k}}{\Delta t} + \frac{2}{\Delta x^2}\right) + c_{k_{i+1}}^{j+1}\left(-\frac{1}{\Delta x^2}\right) = \frac{\Pi_{1_k}}{\Delta t} c_{k_i}^{j} \tag{3}$$

Where j is the time step and Π_{1_k} is the inverse of Fourier number, and is given by

$$\Pi_{1_k} = \frac{1}{Fo} = \frac{{l_k}^2}{D_k t_c} \tag{4}$$

where l_k is the thickness of layer k and t_c is the contact time between film and simulant.

For all nodes between all layers $(k_1; \forall (k \neq 1))$, mass flow of migrants must be the same for layers k and $k+1$,

$$D_k \frac{\partial c_{k_n}}{\partial x} = D_{k+1} \frac{\partial c_{k+1_1}}{\partial x} \tag{5}$$

By expressing the equation in a dimensionless way, applying centered finite differences and knowing that $c_{k_n} = c_{k+1_1}$, the result is

$$c_{k_{n-1}}^{j+1}(-2) + c_{k+1_1}^{j+1}\left(\frac{\Delta x^2}{\Delta t}\left(\Pi_{1_k} + \Pi_{1_{k+1}}\Pi_{2_k}\right) + 2\Pi_{2_k} + 2\right) + c_{k+1_2}^{j+1}\left(-2\Pi_{2_k}\right) = c_{k+1_1}^{j} \frac{\Delta x^2}{\Delta t}\left(\Pi_{1_k} + \Pi_{1_{k+1}}\Pi_{2_k}\right) \tag{6}$$

Where Π_{2_k}

$$\Pi_{2_k} = \frac{D_{k+1}}{D_k}\frac{l_k}{l_{k+1}} \tag{7}$$

For the node that is not in contact with the ambient $(k = 1, i = 1)$, it is assumed that the system is isolated, in other words:

$$\frac{\partial c_{1_1}}{\partial \hat{x}} = 0 \tag{8}$$

Applying centered finite differences:

$$c_{1_1}^{j+1}\left(\frac{\Pi_{1_1}}{\Delta t} + \frac{2}{\Delta x^2}\right) + c_{2_2}^{j+1}\left(-\frac{2}{\Delta x^2}\right) = \frac{\Pi_{1_1} c_{1_1}^{j}}{\Delta t} \tag{9}$$

For the node that is in contact with food $(k = m, i = n)$, convection with the simulant is assumed. This represents an improvement to the model implemented in AKTS-SML, in which only diffusion of the migrant in the simulant is assumed, ignoring the convective effects and therefore underestimating migration. The value of the diffusivity in the previous model is assigned arbitrarily to be $1 \times 10^{-8} m^2/s$, regardless of the nature of the migrant or simulant and the storage temperature. In this paper, using a convective boundary condition is proposed, assuming a convection coefficient that tends to infinity, so the worst case of migration is considered. The equation for this boundary is given by,

$$D_m \frac{\partial c_{m_n}}{\partial x} = h\left(\frac{c_m}{K} - c_\infty\right) \tag{10}$$

Where K is the partition coefficient and is defined as the relationship between migrant concentration in the

polymer and food to reach steady state (11). When K is 1, the migrant is completely soluble in food, thus this is the worst-case scenario.

$$K = \frac{C_p}{C_f} \tag{11}$$

The convection coefficient is h and is considered as a high value, almost infinite.

Since it is unknown how the number of migrants in the simulant (c_∞) evolves, it is necessary to complement the above equation with a balance of the mass flow rate at which the migrant leaves the polymeric packaging with the rate of change of the migrant content in the simulant.

$$A \cdot D_m \frac{\partial c_{m_n}}{\partial x} = \frac{dc_\infty}{dt} V \left(\frac{\rho_{food}}{\rho_n}\right) \tag{12}$$

Where A is the contact area between the package and the food, V is the packaging volume, and ρ_{food} and ρ_n are the densities of the food and the inner layer, respectively.

By expressing the equation in a dimensionless way and using finite differences,

$$c_{m_{n-1}}^{j+1}\left(\frac{1}{\Delta x}\right) + c_n^{j+1}\left(-\frac{\Pi_3}{K} + \frac{\Delta t {\Pi_3}^2}{K(\Pi_4 + \Delta t \cdot \Pi_3)} - \frac{\Delta x}{2}\left(\frac{\Pi_{1_m}}{\Delta t} + \frac{2}{\Delta x^2}\right)\right) = -\frac{\Pi_4 \Pi_3 {c_\infty}^j}{\Pi_4 + \Pi_{3\Delta t}} - \frac{c_n^j \Pi_{1_m} \Delta x}{2\Delta t} \tag{13}$$

Where Π_3 is the Sherwood number and is given by:

$$\Pi_3 = Sh = \frac{h l_m}{D_m} \tag{14}$$

$$\Pi_4 = \frac{V}{A}\frac{\rho_{food}}{\rho_n}\frac{l_m}{t_c D_m} \tag{15}$$

The equations (3), (6), (9) and (13) are assembled into a banded matrix and solved for each time step until t_c is reached. At system startup, it is assumed that each layer has a uniform initial concentration c_k^0.

Finally, the value of migrant content is updated for each time step with:

$${c_\infty}^{j+1} = \frac{1}{(\Pi_4 + \Pi_3 \Delta t)}\left(\frac{c_n^{j+1}\Pi_3 \Delta t}{K} + {c_\infty}^j \Pi_4\right) \tag{16}$$

The nomenclature used in this paper is summarized in Table 1.

Table 1 Nomenclature

k	Layer of a structure
c_{k_i}	Concentration of the migrant in layer k at the node i
D_k	Diffusivity of the migrant in the material of layer k
M_w	Molecular weight of the migrant
T	Storage temperature
D_0, ${A_{p_k}}'$ and τ_k	Parameters of the model (polymer dependents)
j	Time step
Π_{1_k}	Inverse of Fourier number
l_k	Thickness of layer k
t_c	Contact time between film and simulant
K	Partition coefficient
h	Convection coefficient
A	Area between the package and the food
V	Packaging volume
ρ_{food}	Density of the food
ρ_n	Density of the inner layer
Π_3	Sherwood number

Validation

The algorithm described above was compared with the solution given by the finite element software called AKTS-SML, This software uses a diffusion based model for the simulant, therefore, the simulant domain should be discretized as it is done with the structure layers. A structure of a single layer of LDPE with an antioxidant that can migrate to the food was considered. In Table 2, the application data are summarized.

Table 2 Data for model validation

ρ_n(Kg/m^3)	945	M_w(g/mol)	531
${A_p}'$	11.5	c^0 (ppm)	500
τ	0	A(m^2)	0.05
l(μm)	100	V(m^3)	0.001
h	1×10^9 (numeric value to represent an infinite number to over-estimate the migration)		

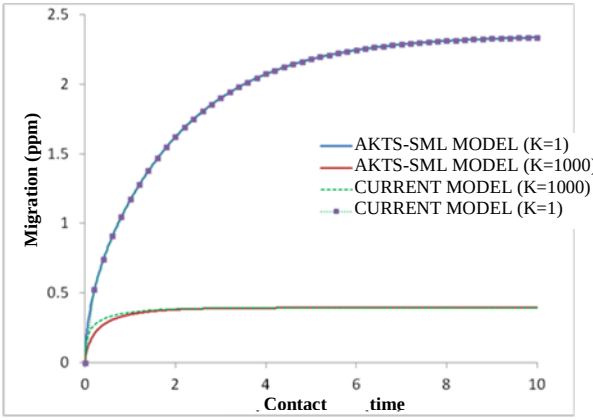

Figure 3 Current model vs. Model implemented in AKTS-SML comparison for different partition conditions

The Figure 3, shows a comparison between the results of current model and AKTS-SML model. It can be seen how, for long periods and low values of the partition coefficient, the results of both models are very similar. For high values of the partition coefficient (low compatibility between the migrant and simulant) the curves differ, particularly in the early days of contact. This happens because, as mentioned above, traditional models assume a diffusive process simulant while our model assumes high convection process, with the intention of being more conservative on these predictions. This assumption would cause migration calculation more demanding in terms of data processing than AKTS-SML model.

Case Study

The structure described in Figure 4 is for packaging sausages. The following regulated substances are associated with the structure:

- M1: Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate
- M2: Tris(2,4-di-tert-butylphenyl) phosphite
- M3: Caprolactam

The information about the package and storage conditions is summarized in Table 3. All these data are input information for actual model.

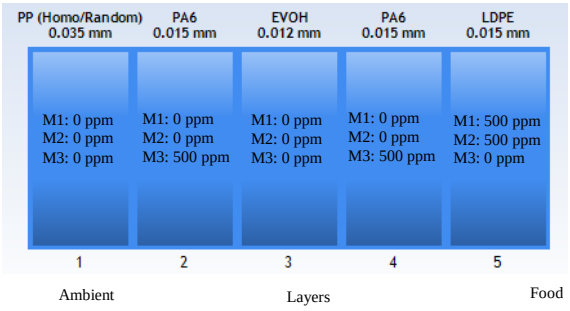

Figure 4 Structure

Table 3 Packaging conditions in the case study

A [m2]	0.02
V [m3]	0.0003
ρ [kg/m^3]	1000
Shelf life temperature [°C]	8
Shelf life [days]	30
K (for each migrant-simulant)	1

The model helps identify the family of the food; in this case, sausages belong to the group *6.03.B: Processed meat products (such as ham, salami, bacon, sausages, and other) or in the form of paste, creams* family, according to EU 10/2011 regulation.

Knowing the family, the program automatically assigns the simulants to be used for migration testing according to the regulation, with its own fat reduction factor (see Table 4).

Table 4 Simulants needed to evaluate the case study structure

Food simulant	Abbreviation	Fat Reduction Factor (FRF)		
		M1	M2	M3
Ethanol 10 % (v/v)	A	1	1*	1*
Acetic acid	D2	4	1*	1*

* 1 is assumed because EU 10/2011 regulation states that it is not necessary to consider the FRF for this migrant

The model identifies that the time and shelf life temperature described in Table 3 correspond to a specific migration test at 20°C and 10 days according to the regulation.

With this information, the model starts to run the numerical algorithm described above. The final result is summarized in Table 5.

According to the results given by the model, for the sausages with the shelf life conditions described in this case study, a structure that would accomplish the specific migration limit requirements given by the European regulation is proposed.

Table 5 Results of the specific migration test analysis of the case study

	Migration results after applying FRF [ppm]		SML [ppm]
	Simulant A	Simulant D2	
M1	4.5871E-004	1.1468E-04	6
M2	4.5869E-004	4.5869E-004	60 **
M3	1.72250E-004	1.7225E-004	60 **

** Overall specific migration is assumed to be 60 ppm, because EU 10/2011 regulation does not state a SML for this substance

Conclusions

The presented model is useful for compliance with EU regulation 10/2011 and other similar regulations on the specific migration of regulated substances. The results of the numerical implementation are comparable to results obtained in other models.

This model has several advantages over others available in the state of art, such as considering in detail all the guidelines of the EU Regulation 10/2011 and the use of a convective boundary condition in the estimation of the migration.

The model intentionally over-predicts the migration, being a model for food safety guarantee, no for accurate prediction.

A web software called Migrasoft® was developed by the ICIPC applying the model presented in this paper [18].

Acknowledgments

The authors gratefully acknowledge the contribution of COLCIENCIAS (Department of Science, Technology and Innovation, Colombia), Universidad EAFIT, the ICIPC and the Colombian company NUTRESA Group for financing and supporting the present applied research work.

References

[1] K. Barnes, R. Sinclair and D. Watson, Chemical Migration and Food Contact Materials, Cambridge: Woodhead Publishing Limited, 2007.

[2] FDA, " Code of Federal Regulations Title 21.," Government Printing Office, Washington D. C, 1991.

[3] C. Europea, "Reglamento UE N° 10/2011 de la comisión de 14 de enero de 2011 sobre materiales y objetos plásticos destinados a entrar en contacto con alimentos.".

[4] Mercosur, "RES. N° 32/10. REGLAMENTO TÉCNICO MERCOSUR SOBRE MIGRACIÓN EN MATERIALES," 2010.

[5] Ministerio de Salud y Protección Social, "Resolución 683 de 2012: "Por medio de la cual se expide el Reglamento Técnico sobre los requisitos sanitarios que deben cumplir los materiales, objetos, envases y equipamientos destinados a entrar en contacto con alimentos y bebidas para consumo humano"".

[6] "EN 1186-3 Materials and articles in contact with foodstuffs - Plastics –Test methods for overall migration into aqueous food simulants by total immersion," 2002.

[7] "EN 1186-7 Materials and articles in contact with foodstuffs - Plastics – Test methods for overall migration into aqueous food simulants using a pouch," 2002.

[8] "EN 1186-9 Materials and articles in contact with foodstuffs - Plastics – Test methods for overall migration into aqueous food simulants by article filling," 2002.

[9] "EN 1186-14 Materials and articles in contact with foodstuffs - Plastics – Test methods for substitute tests for overall migration into iso-octane and 95 % aqueous ethanol," 2002.

[10] S. García, S. Sanches, I. Cooper, R. Franz and P. Paseiro, "Revision of analytical strategies to evaluate different migrants from food packaging materials," *Trends in Food Science & Technology*, pp. 354-366, 2006.

[11] T. Begley, L. Castle, A. Feigenbaum, R. Franz, K. Hinrichs, T. Lickly and P. Mercea, "Evaluation of migration models that might be used in support of regulations for food-contact plastics," vol. 22, pp. 73-90, 2005.

[12] J. Brandsch, P. Mercea, M. Rüter, V. Tosa and O. Piringer, "Migration modelling as a tool for quality assurance of food packaging," vol. 19, 2002.

[13] M. Hamdani, A. Feigenbaum and J. Vergnaud, "Prediction of worst-case migration from packaging to food using mathematical models," vol. 14, 1997.

[14] "Estimation of migration by generally recognized diffusion models in support of EU Directive 90/128/EEC (Migration modelling)," no. Draft CEN-report, CEN/TC194/SC1/WG4 N106, version 1, August 2001.

[15] AKTS_SML. [Online]. Available: http://www.akts.com/sml.html.

[16] Fabes Forshcungs-GmbH, "Migratest(c) Exp," [Online]. Available: http://www.fabes-online.de/software.php?lang=en&mode=migratest.

[17] T. R. Crompton, Additive Migration from Plastics Into Foods: A Guide for Analytical Chemists, Shawbury: Smithers Rapra Technology Limited, 2007.

[18] Migrasoft, ICIPC, 2012. [Online]. Available: http://tools.icipc.org.